

**CARBONATE AND MAGNETITE PARAGENESES AS MONITORS OF CARBON DIOXIDE AND OXYGEN FUGACITY** Andrea M. Koziol, Department of Geology, University of Dayton, 300 College Park, Dayton, OH 45469-2364 USA; e-mail: koziol@neelix.udayton.edu

**Introduction:** A geologist or meteoriticist may have before them an assemblage of minerals that together record a history of the temperature, pressure, and fluid composition that the rock has experienced. Certain key minerals do record water, CO<sub>2</sub>, and O<sub>2</sub> fugacities.

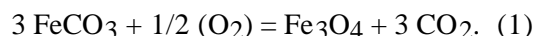
Siderite, FeCO<sub>3</sub>, is one of those key minerals. The stable coexistence of siderite with another key mineral, such as graphite or magnetite (Fe<sub>3</sub>O<sub>4</sub>), is only possible under certain restrictive conditions. If other variables are known, the activity or fugacity of CO<sub>2</sub> or O<sub>2</sub> in the fluid phase once present in the rock can often be estimated. This is an oxybarometer: a way of estimating oxygen fugacity (fO<sub>2</sub>) from mineral assemblages. The results can be used to understand parageneses of iron-rich carbonate and iron oxide minerals, as seen in Mars materials, certain chondrite meteorites and banded iron formations on Earth. We potentially could unlock the history of changing CO<sub>2</sub> and O<sub>2</sub> fugacity during the early history of several planetary bodies.

**ALH84001:** An intriguing occurrence of siderite-rich carbonate is in ALH 84001, a Martian meteorite that has been suggested to contain evidence of former life [1]. Leaving aside the question of former life on Mars, the carbonates may still provide a record of past near-surface conditions on Mars. The carbonate rosettes are small, with a variable composition, from Ca-rich cores (almost dolomite-ankerite in composition) through Fe-rich magnesite compositions, to magnesite-rich mantles or rims, often with iron-rich rims on the outside. The occurrence of small magnetite grains in the carbonates of ALH 84001 and their origin is a hotly debated topic. These magnetite grains have been variously interpreted as magnetosomes of biological origin [1 – 3], vapor-phase condensation [4], or a by-product of siderite decarbonation [5].

**Inorganic origin of minute magnetite grains:** Brearley [5] examined the magnetite grains in the porous carbonate with TEM and confirmed the observations of McKay et al. [1]. Many small voids, closely associated with the

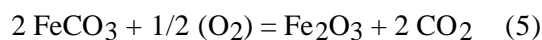
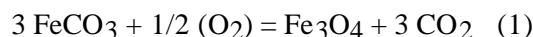
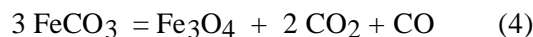
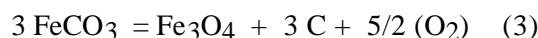
magnetite grains, led Brearley to suggest that a later reheating event caused the carbonate to decompose. The CO<sub>2</sub> evolved would produce the small voids. The siderite component of the carbonate would preferentially break down, forming magnetite [5].

Alternatively, an increase in oxygen fugacity would promote magnetite formation by



Oxygen fugacity could change as pore fluid changes, or as certain mineral reactions progress. The oxygen may not be present in a gas phase, but may be dissolved in a fluid or supplied by a mineral. Calculated oxygen fugacities for rocks and fluids on the Earth are often vanishingly small (10<sup>-10</sup> to 10<sup>-70</sup> bars). Yet this is an extremely important parameter. It is recorded in rocks by the changing oxidation state of iron, manganese, and other elements and the presence or absence of certain minerals. With increasing oxygen fugacity, metallic iron changes to ferrous and then ferric iron compounds including wüstite (FeO), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>). Similarly, the decarbonation limit of siderite changes with increasing oxygen fugacity. (The stability of CO<sub>2</sub> itself depends on oxygen fugacity. Carbon dioxide actually requires somewhat oxidizing conditions.)

The siderite decarbonation limits are listed below, in order from low to higher fO<sub>2</sub>:



Another important relationship in this system is:

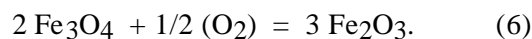


Figure 1 displays these relationships graphically. Curve (3) shows how reaction (3) depends on temperature and oxygen fugacity, curve (5) is the trace of reaction (5) and so on.

The stable coexistence of siderite + magnetite, or siderite + magnetite + graphite, or siderite + hematite, implies a certain oxygen fugacity was experienced by the rock. Of course, reactions (2) through (5) also depend on total pressure and temperature. These variables need to be known to compute a value for  $\text{CO}_2$  or  $\text{O}_2$  fugacity.

**Example:** An example of this type of analysis can be done in a crude way with the information at hand. Detailed descriptions of the ALH 84001 meteorite [1,4] do not mention any coexisting elemental iron, graphite, or hematite with or within the carbonate rosettes, only magnetite. Analysis by carbon-XANES would be able to detect minute particles of graphite, but none are reported [7]. This limits the range of possible temperatures and oxygen fugacities (at one bar  $\text{CO}_2$  pressure) experienced by the carbonates to those between the curve (6) and curve (3) in figure 1.

If temperature is known, an oxygen fugacity for this assemblage can be estimated. Note that only a restricted range of temperatures and oxygen fugacities are possible at the assumed pressure of 1 bar. This range shrinks or expands as  $\text{CO}_2$  pressure decreases or increases, respectively. This diagram is based on the work of Yui [8] using thermodynamic data of that era. It is unclear what the accuracy and precision are for these estimates.

**References:** [1] McKay, D.S., *et al.*, (1996) *Science* 273, 924-930. [2] Thomas-Keptra, K.L., *et al.*, (1998) *LPSC XXIX* (CD-ROM), Abstract # 1494. [3] Thomas-Keptra, K.L., *et al.*, (1999) *LPSC XXX* (CD-ROM), Abstract # 1856. [4] Bradley, J.P. *et al.* (1998) *LPSC XXIX* (CD-ROM), Abstract # 1757. [5] Brearley, A.J. (1998) *LPSC XXIX* (CD-ROM), Abstract # 1451. [6] Mittlefehldt, D.W., (1994) *Meteoritics* 29, 214-221. [7] Flynn, G.J., *et al.* (1998) *LPSC XXIX* (CD-ROM), Abstract # 1156. [8] Yui, S. (1966) *Econ. Geol.*

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**Figure:** Stability fields of hematite, magnetite, siderite, and graphite at 1 bar  $\text{CO}_2$  pressure over a range of temperatures and oxygen fugacities. Curve (6): the magnetite-hematite equilibrium (reaction 6). Curve (3):  $3 \text{FeCO}_3 = \text{Fe}_3\text{O}_4 + 3 \text{C} + 5/2 (\text{O}_2)$  (reaction 3). Siderite and magnetite assemblages are stable only in the area between curves (6) and (3). Curve (1):  $2 \text{FeCO}_3 + 1/2 (\text{O}_2) = \text{Fe}_2\text{O}_3 + 2 \text{CO}_2$  (reaction 1). Line (4): the upper limit of siderite stability at this  $f\text{CO}_2$  (reaction 4).

